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INTERACTION OF HYDROGEN WITH ALKALI METAL-ADDED ACTIVE CARBON AS REVEALED BY ESR

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Coconut carbon adsorbed with sodium or potassium vapor gives an ESR band at g=2.004 or 2.007 which diminishes on introduction of hydrogen, and catalyzes the H_2-D_2 exchange reaction, whereas the coconut carbon itself gives no such ESR and the catalytic activity.

Some free radicals have been detected on carbon, while they are usually formed by bond breakage round the edge of the condensed carbon rings and disappear by high temperature heat treatment.[1)]

It has been reported that the sugar charcoal prepared at relatively low temperatures exhibits a catalytic activity for the ortho- para hydrogen conversion which can be correlated with the electron spins as determined by ESR.[2)]

The conventional active carbon which is usually produced by steam treatment at high temperature has no activity for the H_2-D_2 exchange reaction. However it has been found that it is activated for the exchange reaction by adsorption of sodium or potassium vapor. Since an electron donation from alkali metal to carbon is expected, ESR spectra of active carbon adsorbed with alkali metal has been investigated. It has been found that there are unpaired electrons which interact with hydrogen on the alkali-added active carbon.

The active carbon sample was a coconut carbon obtained from the Daiichi Tanso Co. It was throughly washed with distilled water to remove electrolytes and used in a form of powder. The addition of alkali metals were made by adsorption of the metal vapor at 400°C followed by circulation of helium gas for 5 hrs. The added alkali metal was distirubuted over the carbon surface during the circulation of helium. The alkali-added carbon was transferred into ESR tube in dry nitrogen atmosphere.

The H_2-D_2 exchange reaction did not take place at room temperature over the active carbon itself preevacuated at 400°C for 2 hr. The rate of H_2-D_2 exchange reaction at 0°C was 25.4 mlSTP/min over 1 gram of the active carbon adsorbed with 297 mg of potassium under 21.1 cmHg of H_2-D_2 gas.

The ESR spectra were obtained in vacuum at g=2.007 with the potassium-carbon and g=2.004 with the sodium carbon as shown in Fig. 1 and 2 respectively. No spectrum was observed with the active carbon itself at room temperature. It is clear that the ESR spectrum is caused by the addition of potassium or sodium. On intro-

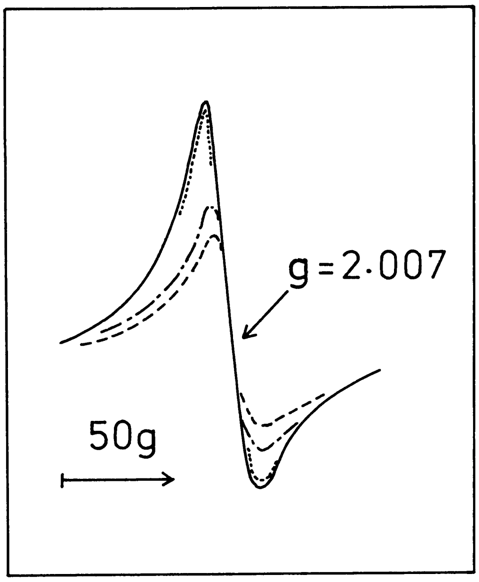

Fig. 1 ESR spectra of potassium-added active carbon

———— without H_2
—·—·— 5 min after introduction of H_2
- - - - - 30 min after introduction of H_2
·········· after evacuation at 100°C for 2 min

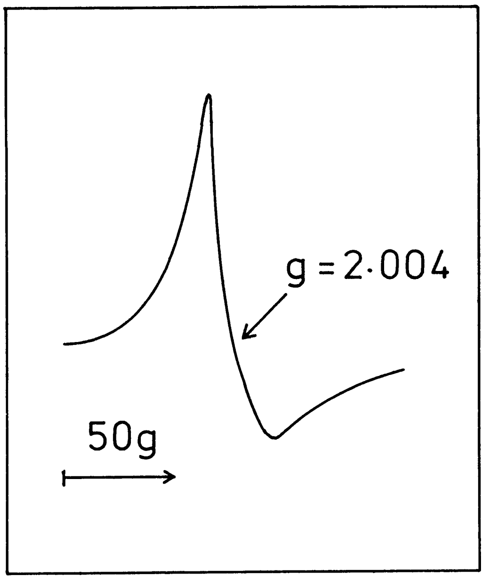

Fig. 2 ESR spectrum of sodium-added active carbon

duction of hydrogen of 40 cmHg, the spectrum was decreased to the dotted line after 30 min and remained at the low level after evacuation for 30 min at room temperature but regained the original spectrum after evacuation at 100°C for 2 min as shown in Fig. 1. Since the g-factor of the ESR is close to that of free electron and the ESR appears on addition of the electron donor, the ESR is ascribable to the unpaired electrons trapped in the carbon matrix. It is suggested that these unpaired electrons interact with hydrogen forming an active species (possibly H^-) for the H_2-D_2 exchange reaction because the activity is simultaneously developed by the addition of alkali metal. The spin concentration of the alkali-added carbon as determined by calibration with DPPH were as follows.

Carbon-K	(32 wt%)	1.2×10^{17}/g-carbon
Carbon-Na	(8.4 wt%)	4.9×10^{17}/g-carbon

References

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